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Cobalt(III) and Chromium(III) Complexes with Ethylenediaminemonoacetic Acid*1

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Cobalt(III) and chromium(III) complexes with ethylenediaminemonoacetic acid (EDMA), $[Co(edma)_2]Cl \cdot 2H_2O$ and $[Cr(edma)_2]Cl \cdot 3H_2O$, (edma: $H_2NCH_2CH_2NHCH_2COO^-$), were prepared. The former complex was isolated as two geometrical isomers. From the electronic absorption spectra, the two isomers were assigned to *trans* and *cis* forms with respect to the carboxylate oxygen atoms coordinated. Chromium(III) complex was concluded to have the *trans* form by comparing the IR spectrum with those of the above two isomers of cobalt(III) complexes.

Terdentate chelating ligands can take various coordination forms in octahedral environment, depending upon the steric requirements of the ligands and the character of the central metal ion, especially upon the kind of coordination sites the ligands contain. As typical representatives of the terdentate ligands of (N,O,O)-, (N,N,O)- and (N,N,N)-types, iminodiacetic acid, ethylenediaminemonoacetic acid (abbreviated as EDMA)[1] and diethylenetriamine can be chosen.

In the present work EDMA, a simple, artificial and basic amino acid, was selected as the terdentate ligand. There are only a few reports[2,3] on the metal complexes with EDMA. In order to in-

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1) T. Goldschmit, *Ger.*, **819**, 402 (1951).
2) M. A. Doran, *Anal. Chem.*, **33**, 1752 (1961).
3) M. Idelson, I. R. Karady, B. H. Mark, D. O. Rickter and V. H. Hooper, *Inorg. Chem.*, **6**, 450 (1967).

vestigate the stereochemistry of the complexes, the following two purposes were presented: (1) preparation of the EDMA complexes of cobalt(III) and chromium(III) ions, and (2) approach to the structures of the complexes by comparing their electronic and IR spectra with those of the related complexes.

Experimental

Preparation of the Complexes. *1) trans-Bis-(ethylenediaminemonoacetato)cobalt(III) Chloride Dihydrate, trans*-[Co(edma)$_2$*[3]]Cl·2H$_2$O (I). 25.2 g (0.12 mol) of ethylenediaminemonoacetic acid dihydrochloride monohydrate (Hedma·2HCl·H$_2$O) was dissolved into 50 m*l* of water and the solution was neutralized with 20 g (0.24 mol) of sodium hydrogencarbonate. To this solution was added a solution of 10.4 g (0.044 mol) of cobalt(II) chloride hexahydrate in a very small amount of water and 10 m*l* of hydrogen peroxide (10%), and the mixture was warmed on a water bath to nearly 40°C. After the solution was evaporated to about 60 m*l*, an equal volume of ethanol was added to the resulting solution. The solution was kept in a refrigerator. Reddish purple crystals were separated out and recrystallized from 50% ethanol solution. Yield, 5.2 g (32.5%).

Found; C, 26.04; H, 5.87; N, 15.78%. Calcd for [Co(edma)$_2$]Cl·2H$_2$O: C, 26.34; H, 6.09; N, 15.36%.

2) cis-Bis(ethylenediaminemonoacetato)cobalt(III) Chloride Dihydrate, cis-[Co(edma)$_2$]Cl·2H$_2$O (II). To a solution of hexaamminecobalt(III) chloride (5.4 g, 0.02 mol), 9.4 g (0.045 mol) of Hedma·2HCl·H$_2$O was added and the mixture was warmed to nearly 70°C on a water bath. Potassium hydroxide (6.7 g) in 200 m*l* of water was added slowly to the solution, which was warmed, until the odor of ammonia vanished. After adjusting the pH of the solution to 7 with hydrochloric acid, an equal volume of ethanol was added to the resulting solution. After cooling to 0°C, orange yellow crystals were separated out and recrystallized from the aqueous solution. Yield, about 2.1 g (28.8%).

Found: C, 25.75; H, 6.15; N, 15.19%. Calcd for [Co(edma$_2$)]-Cl·2H$_2$O: C, 26.34; H, 6.09; N, 15.36%.

An orange yellow complex of cobalt(III) of *cis* form was also prepared by using cobalt(II) chloride hexahydrate as the starting material in an aqueous solution at high temperature.

3) trans-Bis (ethylenediaminemonoacetato) chromium (III) Chloride Trihydrate, trans-[Cr(edma)$_2$]Cl·3H$_2$O (III). Two isomers, *cis* and *trans* forms of the cobalt(III) complexes could be prepared by suitably selecting the starting materials as described above, in 1) and 2).[4] However, in the case of chromium(III) complexes, it was impossible to prepare the *cis* form even by starting from hexaamminechromium(III) iodide in a manner similar to that used in the preparation of the corresponding cobalt(III) complex in 2).

Only the *trans* form was obtained for the chromium-(III)-EDMA system. To a solution of 5.3 g (0.02 mol) of chromium(III) chloride hexahydrate in a small amount of water, Hedma·2HCl·H$_2$O (9.2 g, 0.044 mol) was added and the mixture was heated on a water bath. After adjusting the pH of the solution to 7, an equal volume of ethanol was added to the resulting solution. When it was cooled to 0°C, red crystals were separated out and recrystallized from 10% ethanol solution. Yield, 5.5 g (72.5%).

Found: C, 25.47; H, 6.46; N, 15.42%. Calcd for [Cr(edma)$_2$]Cl·3H$_2$O: C, 25.57; H, 6.40; N, 14.91%.

Preparation of Ligand. *Ethylenediaminemonoacetic Acid Dihydrochloride Monohydrate*, Hedma·2HCl·H$_2$O. The solution of 94.5 g (1 mol) of monochloroacetic acid in 100 m*l* of water was neutralized with 84 g (1 mol) of sodium hydrogencarbonate, and 60 g (1 mol) of ethylenediamine (98%) was added to the solution. After being added 40 g of sodium hydroxide in 80 m*l* of water, the mixture was acidified with 6N hydrochloric acid and the solvent was then evaporated off. After filtration, ethanol three times in volume was added to the filtrate, when the oilish liquid was produced. This syrupy substance was treated by separating funnel and then concentrated hydrochloric acid was added to the syrup. After being added the mixture of ethanol and ether to the solution, it was kept in a refrigerator for a day. White crystals were separated out and recrystallized from 50% ethanol solution. The method is new and simple for the preparation of the ligand material. Yield, 140 g (70%).

Found: C, 22.94; H, 6.72; N, 12.96%. Calcd for C$_4$H$_{10}$N$_2$O$_2$·2HCl·H$_2$O: C, 22.97; H, 6.76; N, 13.50%.

Results and Discussion

Electronic Absorption Spectra. The visible absorption spectra for all the complexes in aqueous solutions are shown in Figs. 1 and 2, together with those of *cis*-[Co(edda)*[4](en)]Cl·3H$_2$O, *trans*-[Co-(edda)(en)]NO$_3$·H$_2$O[5] and [Cr(ox)(en)$_2$]I[6] for

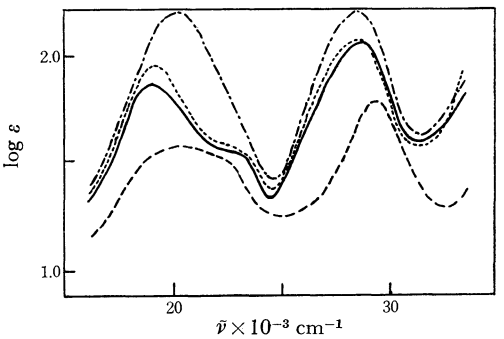

Fig. 1. Electronic absorption spectra: (———) *trans*-[Co(edma)$_2$]Cl·2H$_2$O, (– – – –) *cis*-[Co(edma)$_2$]-Cl·2H$_2$O, (· · · · · · · ·) *trans*-[Co(edda)(en)]NO$_3$·H$_2$O and (—·—·—) *cis*-[Co(edda)(en)]Cl·3H$_2$O.

*3 edma is an abbreviated form of $H_2NCH_2CH_2NHCH_2COO^-$.

*4 edda is an abbreviation of $^-OOCCH_2NHCH_2CH_2NHCH_2COO^-$.

4) M. Mori, M. Shibata, E. Kyuno and M. Kanaya, This Bulletin, **34**, 1837 (1961).

5) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

6) H. L. Schlaefer, O. King, L. Mahler and H. P. Opitz, *Z. Phys. Chem.*, **24**, 307 (1960).

Table 1. Absorption maxima ($\times 10^3$ cm^{-1})

Complex	Band Ia $\bar{\nu}$ (log ε)	Band Ib $\bar{\nu}$ (log ε)	Bnad II $\bar{\nu}$ (log ε)
trans-[Co(edma)$_2$]Cl·2H$_2$O	18.87 (1.88)	22.03 (sh)	28.17 (2.05)
cis-[Co(edma)$_2$]Cl·2H$_2$O	20.00 (1.59)	21.51 (1.58)	28.90 (1.77)
trans-[Cr(edma)$_2$]Cl·3H$_2$O	19.80 (1.84)	21.70 (sh)	26.32 (1.88)
trans-[Co(edda)(en)]NO$_3$·H$_2$O[5]	18.90 (1.94)	22.32 (sh)	27.62 (2.05)
cis-[Co(edda)(en)]Cl·3H$_2$O[5]	18.05 (sh)	20.20 (2.23)	27.78 (2.23)
[Cr(ox)(en)$_2$]I[6]	20.33 (1.81)		27.17 (1.83)

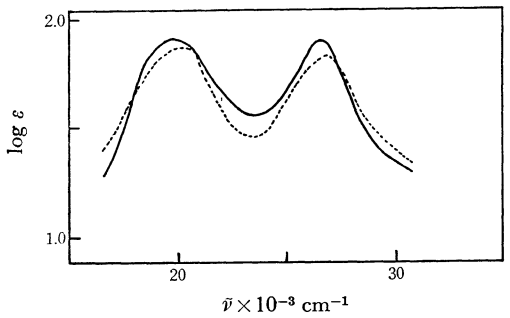

Fig. 2. Electronic absorption spectra: (———) *trans*-[Cr(edma)$_2$]Cl·3H$_2$O and (--------) [Cr(ox)-(en)$_2$]I.

comparison. Numerical values concerning their absorption maxima are given in Table 1.

The spectrum of complex I has a band which is remarkably split into two components Ia and Ib, at 18.9 and 22.0 (shoulder). It has another band at 28.2×10^3 cm^{-1}. The shape of the spectrum and the positions of the absorption peaks are in close agreement with those of *trans*-[Co(edda)(en)]-NO$_3$·H$_2$O.

The possible chelate configurations in six geometrical isomers of [M(edma)$_2$]$^+$-type complex and those in two isomers of [Co(edda)(en)]$^+$ complex are given in Figs. 3 and 4, respectively. It is possible to assume from the appearance of the splitting in the first bands of both complex I and *trans*-[Co(edda)(en)]$^+$ in Fig. 1 that the structure of complex I has either configuration (a) or (b) in Fig. 3, which has *trans* configuration with respect to the coordinated carboxylate oxygens.[7,8] However, the choice of (a) or (b) for the structure of complex I is not clear.

The spectrum of complex II has a broad first band, which is slightly split into two components Ia and Ib of nearly equal intensity, at 20.0 and 21.5, and a second band at 28.9×10^3 cm^{-1}.

The spectrum of complex II does not completely agree with that of *cis*-[Co(edda)(en)]$^+$ ion. A slight splitting of the first band makes us believe that complex II has a structure of *cis* configurations.

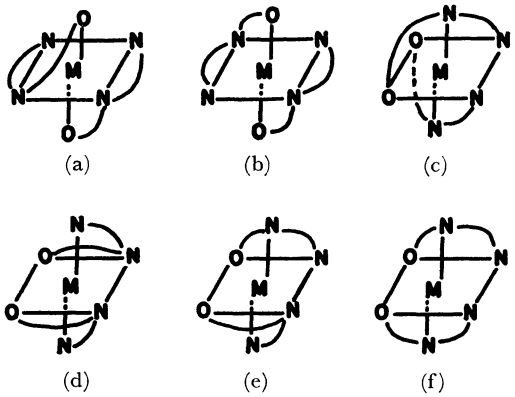

Fig. 3. The possible six geometrical isomers of bis(ethylenediaminemonoacetato)cobalt(III) and chromium(III) ion:
(a) *trans,cis,cis* (with respect to carboxylate oxygen, primary amine nitrogen and secondary amine nitrogen) (b) *trans,trans,trans*, (c) *cis,cis,trans*, (d) *cis,trans,cis*, (e) *cis,cis,cis*, (f) *cis,cis,trans*.

Fig. 4. The possible two geometrical isomers of [Co(edda)(en)]$^+$: (g) *trans* form, (h) *cis* form (with respect to carboxylate oxygen atoms).

However, the choice of (c), (d), (e) or (f) for the structure of complex II can not be done easily, as they have identical coordination forms except for the difference of the chelating features as seen in Fig. 3.

The spectrum of complex III shows the first band at 19.8 with a small shoulder at 21.7 and the second band at 26.3×10^3 cm^{-1}. On the other hand, the spectrum of [Cr(ox)(en)$_2$]I[5] shows two bands at 20.3 and 27.1×10^3 cm^{-1} with no shoulder near the first band. Since the shoulder at 21.7×10^3 cm^{-1} in complex III is thought to be one of the components of the first band, its configuration is assumed to be *trans* form.

IR Spectra. The infrared absorption spectra

7) J. Hidaka, Y. Shimura and R. Tsuchida, This Bulletin, **35**, 567 (1962).
8) H. Yamatera, *ibid.*, **31**, 95 (1958).

of the three new complexes synthesized were measured in the nujol mull state in the range 4000—700 cm^{-1}. Since the strong band appearing at 1730 cm^{-1}, which is assigned to free carboxylic acid in the ligand itself, is found to be shifted to 1630 cm^{-1} in cobalt(III) complexes and to 1645 cm^{-1} in chromium(III) complex, it is obvious that all the carboxylate groups are coordinated to central metal ions in all the three complexes.[9]

Though all the complexes show very similar spectra, the bands appearing at 1220 cm^{-1} (assigned to C–CN stretching vibration)[4] and at 1040 cm^{-1} (assigned to NH_2 twisting)[4] are split into two bands in the case of complexes I and III but not in II. Appearance of the splitting in IR spectra in complexes I and III also supports the conclusion that both complexes I and III have *trans* configuration with respect to the coordinated carboxylate oxygen atoms, since the splitting is observed in the first band of the electronic spectra.

9) D. H. Bush and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **75**, 4574 (1953); *ibid.*, **78**, 716 (1956).